

COMPARATIVE STUDY OF TWO COMMERCIAL STONEWARE PASTES FOR PLASTIC SHAPING BY POTTERY WHEEL

Réka BARABÁS^a, Oana CADAR^b, Liliana BIZO^{c,*}

ABSTRACT. Two commercial stoneware pastes traditionally used to produce ceramic objects were evaluated. The objective was the comparative characterization of the pastes and to find the most suitable to obtain fine ceramic objects using the pottery wheel. Both ceramic pastes were characterized by X-ray powder diffraction (XRPD), particle size analyses (laser diffraction) and thermal analyses (thermogravimetry-TG, its derivative-DTG, and differential thermal analysis-DTA). The technological properties like linear drying and firing shrinkage, moisture content and plasticity were also determined. The results showed that both pastes have appropriate properties making them suitable for plastic shaping by pottery wheel. In addition, the stoneware paper clay paste is “greener” due to its content of cellulose fibers which can come even from recycled paper.

Keywords: *traditional ceramics, commercial stoneware, XRPD, TG-DTG-DTA, drying and firing shrinkage, moisture content, plasticity, potter’s wheel*

INTRODUCTION

Traditional ceramics refers to ceramic products that are produced from unrefined clay and combinations of refined clay and powdered or granulated non plastic minerals. Often, traditional ceramics is used to refer to ceramics in which the clay content exceeds 20 % [1, 2]. The major ceramic

^a Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Department of Chemistry and Chemical Engineering of Hungarian Line of Study, 11 Arany Janos str., RO-400028, Cluj-Napoca, Romania

^b INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath str., RO-400293, Cluj-Napoca, Romania

^c Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Department of Chemical Engineering, 11 Arany Janos str., RO-400028, Cluj-Napoca, Romania

* Corresponding author: liliana.bizo@ubbcluj.ro



categories are earthenware, stoneware and porcelain. Stoneware bodies are composed of modified secondary clays, fired to high temperatures of 1200 to 1300 °C to produce a vitrified, hard, and durable ceramic. It is made from clay but is more durable than other kinds of pottery and earthenware. The porosity of stoneware is < 3 % and colours include white, buff, grey and black. Stoneware has a reputation for being easy to use, is generally quite plastic, workable, and versatile. Some stoneware clay feels quite smooth and silky to use. However, if it is added grog or sand, it can feel coarser and grittier. Grog is clay that has previously been fired and then crushed; it comes in different particle sizes, and it's usually added to clay to give it a different texture and reduce the shrinkage of the piece [3].

The main phases in ceramics technology are: (I) preparation of the ceramic mass; (II) shaping; (III) drying; (IV) firing; and (V) finishing the product. Many shaping/forming methods are used for ceramic products, and these can be grouped into three basic categories: powder compaction (dry pressing, hot pressing, cold isostatic pressing, etc.), casting (slip casting, gel casting, electrophoresis casting, etc), plastic forming (extrusion, injection molding, etc.) [4]. In case of the traditional ceramics there are some manual shaping methods, which belongs to the plastic forming, like: pinching, coiling, or using a potter's wheel [5, 6]. There is a wide variety of clays on the market for potter's wheel and all have their own properties that make them suitable than others for specific projects. Given the fact that in the technology of artisanal ceramics there are several shaping methods, the question arises, which of the commercial clays is the most suitable for shaping on the potter's wheel?

In this study, two commercial stoneware pastes with different compositions were compared. The first studied paste was a Stoneware B17C (noted S1) (Valentine Clays Ltd, Stoke-on-Trent, UK) [7]. This paste is a blend of selected low iron clays providing an ideal background for a decorative approach to stoneware ceramics. Silica sand makes it excellent for throwing, too [7]. The second one, PCL stoneware paperclay (noted S2) (SIO-2®, Esparreguera-Barcelona, Spain) [8], consists of a mixture of clay and cellulose fibers. The cellulose fibers in paperclay can come from either new or recycled paper pulp, derived from plants such as cotton, hemp, flax, linen, or trees [9]. By adding paper to the clay potters the number of defects could be reduced. Because paperclay is so strong at the greenware stage, it can be used in a technique called "raw glazing". In addition, the stoneware paper clay body with 30% impalpable grog (up to 80 Mesh) is formulated for artistic ceramics and it is unique for modelling, due to its exceptional plasticity [8]. It is especially suitable for making impossible shapes with difficult drying. The presence of paper fibers inside avoids formation of cracks and problems of deformations and leads PCL clay to surprising artistic possibilities [8].

Since the knowledge of a material's properties is the basis of materials science and is a necessity in the development of viable technical solutions, the objective of this work was the characterization of two commercial stoneware pastes and to find the most suitable to obtain fine ceramic objects by plastic shaping using pottery wheel. The properties which have been considered in the present study are drying or firing shrinkage, moisture content and plasticity. Moreover, XRPD and TG-DTG-DTA analysis were employed to determine the mineralogical composition, before and after firing, and thermal behavior of the studied stoneware pastes.

RESULTS AND DISCUSSION

Particle size distribution (PSD) analyses

The particle size distribution (PSD) in a ceramic body has a significant impact on the packing efficiency, which in turn, influences the size and shape of pores, the shrinkage behavior and microstructure development [10]. The PSD of the S1 and S2 stoneware pastes in suspension were analyzed by laser diffraction and the results are given in Figure 1(a, b). It can be observed from Figure 1(a) that S1 shows a wide trimodal distribution presenting three maximum points, which are centered at around 0.15, 3 and 30 μm , respectively. For the S2 sample (Figure 2(b)) the results show a narrow distribution with fractions ranged from 0.01 and 0.03 μm . The results for PSD analyses are summarized on Table 1.

As visible from the results, the S2 paste contains finer particles, with a mean value of 0.021 μm , whereas larger particles were found for the S1 paste, with a mean value of 2.382 μm . It is known that the finer the particles, the larger the surface they can expose to water and, consequently, the higher the plasticity.

Mineralogical composition

The mineralogical transformations which take place during the firing process are very important for establishing the final properties of the ceramic products. Consequently, the mineralogical transformations caused by firing, of two different compositions used in the formulation of ceramic pastes have been studied by XRPD. Figure 2 (black line) shows the XRPD pattern of the S1 ceramic paste.

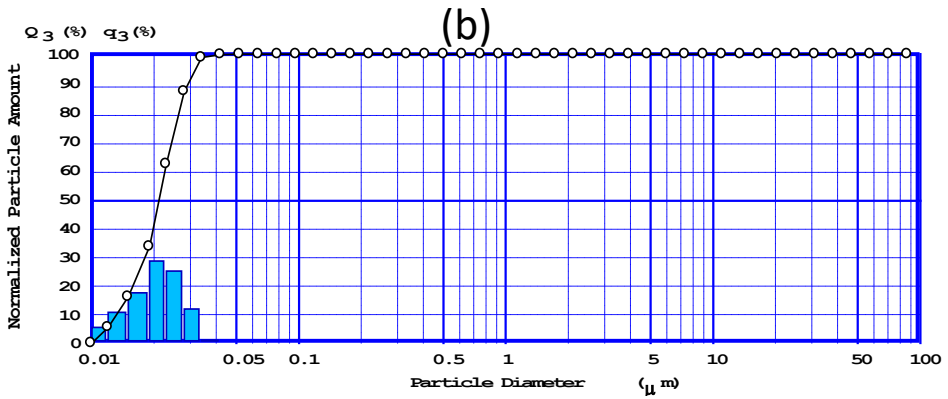
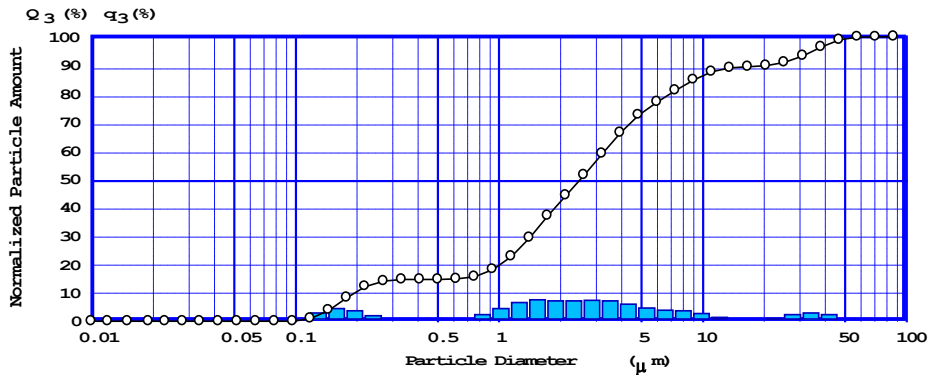


Figure 1. PSD of S1 and S2 stoneware samples.

Table 1. The results of PSD analyses performed on S1 and S2 stoneware pastes

Sample ID	Median D (μm)	Modal D (μm)	Mean V (μm)	SD*	D ₂₅ (μm)	D ₅₀ (μm)	D ₇₅ (μm)
S1	2.503	1.562	2.382	0.640	1.227	2.503	5.433
S2	0.021	0.021	0.021	0.126	0.017	0.021	0.025

* SD-standard deviation

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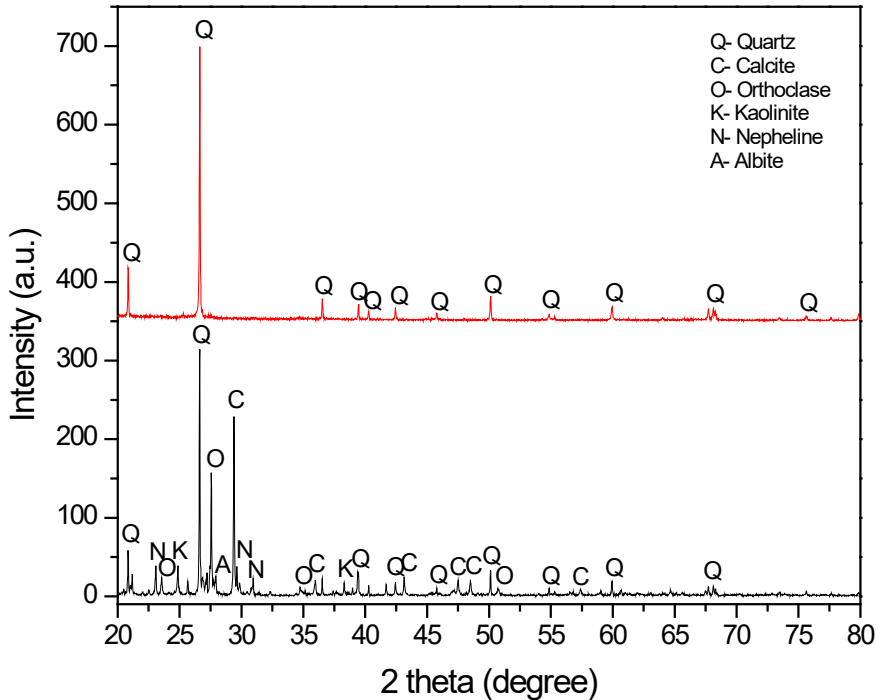


Figure 2. XRPD patterns of S1 sample (black) before and (red) after thermal treatment at 1260 °C.

The sample is mainly constituted of quartz (SiO_2), calcite (CaCO_3), orthoclase (KAlSi_3O_8), albite ($\text{NaAlSi}_3\text{O}_8$). The main clay mineral is kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). In addition, some traces of nepheline ($(\text{Na},\text{K})\text{AlSiO}_4$) were also identified. The XRPD diffractogram of the ceramic body fired at 1260 °C is shown in Figure 2 (red line). After firing the crystalline phase identified was quartz (SiO_2).

Jordán et al. stated before that the sintering temperature for firing ceramic pastes exceeds the energy threshold of the reactivity of the materials and produces a series of reactions and transformations that lead to the formation of new phases and the disappearance of others [11].

In Figure 3 are shown the XRPD patterns of the S2 ceramic paste before (black line) and after firing (red line) at 1320 °C. In this case the sample is mainly constituted of quartz (SiO_2), and kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). The XRPD diffractograms of the ceramic bodies sintered at 1320 °C are shown in Figure 3. After firing the identified phases were quartz (SiO_2), and mullite.

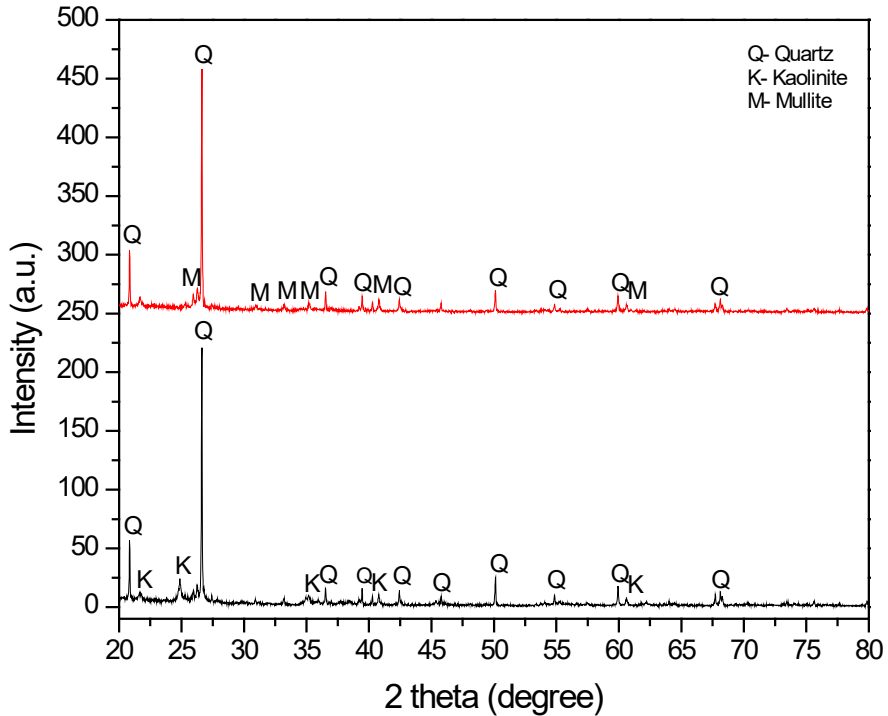


Figure 3. XRPD patterns of S2 sample (black) before and (red) after thermal treatment at 1260 °C.

It was previously demonstrated that mullite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ to $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) is an important crystalline phase which is desirable to be present in ceramics, due to its properties like low thermal expansion and thermal conductivity, creep resistance and high temperature stability [12]. In addition, quartz is known to prevent warping of the fired materials [13].

Thermal analyses

Generally, during the firing process, a series of intercrystalline and extracrystalline reactions take place like: (I) dehydroxylation of clay minerals and the consequent formation of pseudo-amorphous products (such as metakaolinite from kaolinite dehydroxilate product); (II) crystallisation of primary mullite from pseudo-amorphous products with a consequent segregation of a silica rich amorphous phase; (III) formation of an alkaline melt originating from the melting of feldspar; (IV) viscous sintering, or vitrification, in which the viscous melt fills up the pores in the body under the

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influence of capillary forces so that a dense body is obtained; (V) partial decomposition of quartz due to instability in the presence of the alkaline melt; (VI) crystallisation of secondary mullite [14].

Thermal behavior of the S1 stoneware is presented in Figure 4, where the obtained TG, DTG and DTA curves are displayed. Through the obtained data, information about the presence of hygroscopic water, chemical water, carbonates (calcite), decomposition of organics, solid phase transformation and polymorphic changes can be obtained by their characteristic endothermic or exothermic responses at different temperature ranges [15-17]. For S1 ceramic paste ~ 20 wt% of mass loss corresponding to surface water (30-100 °C) can be observed. The chemical water mass loss (200-500 °C) was around ~ 1 wt%.

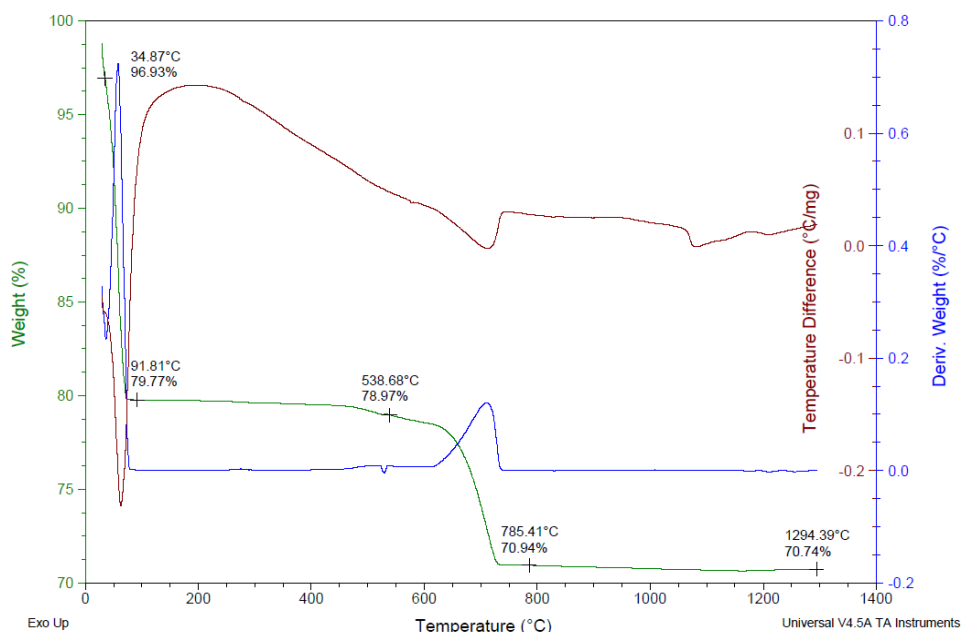


Figure 4. Thermogravimetry (TG- green), its derivative (DTG-blue) and differential thermal analysis (DTA- red) curves of S1 stoneware paste.

The $\alpha \rightarrow \beta$ quartz transformation for the S1 paste was observed in the DTA curve, with the small endothermic minimum at 570 °C [18]. Above ~ 600 °C, the decomposition of calcite started, corresponding to the endothermic peak with the minimum in the DTA curve at 700 °C (Figure 4), overlapping

with the dehydroxylation processes of clay minerals also occurring at these temperatures. Upon heating up to 1300 °C, the total mass loss for the S1 paste was ~ 20 %. The total mass loss was 29.26%.

Figure 5 revealed the results of thermal analysis for the S2 ceramic paste. The mass loss corresponding to surface water (25-100 °C) can be observed; this was ~ 14.73 wt%. The chemical water mass loss (400-600 °C) was around ~ 4.5 wt%. As temperature increased (~ 985 °C) the primary mullite formation process was evidenced by means of a small exothermic peak, and finally, secondary mullite formation, usually detected by a couple of exothermic small peaks in the 1100-1240 °C range was scarcely detected in the studied S2 paste. For the S2 paste the total mass loss was 20.52%.

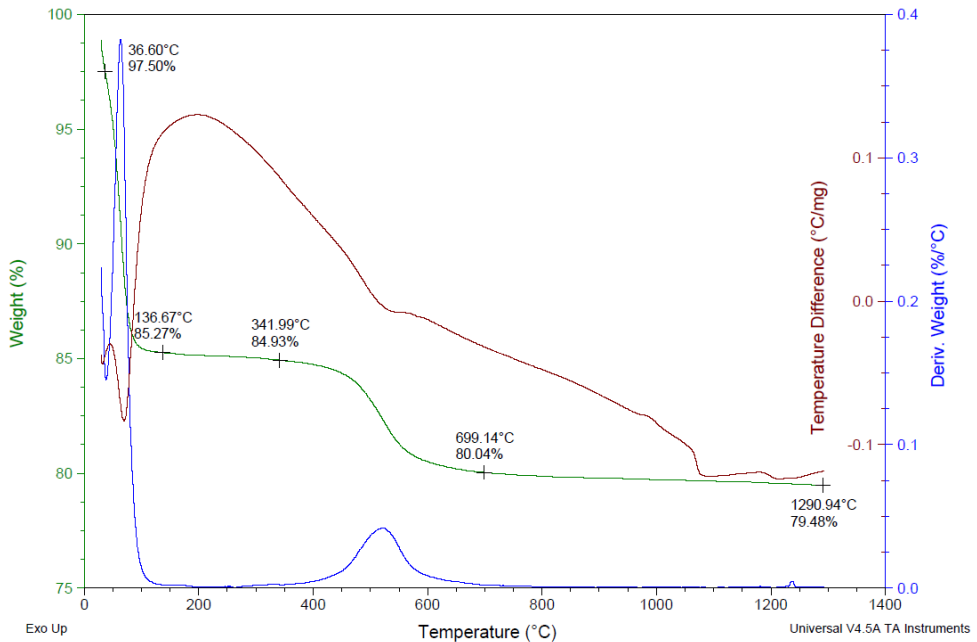


Figure 5. Thermogravimetry (TG- green), its derivative (DTG-blue) and differential thermal analysis (DTA- red) curves of S2 stoneware paste.

Plasticity measurements

Plasticity is the outstanding property of clay-water systems. The shaping of ceramic products by plastic processes is based on the plasticity of the mass, therefore it is important to know it. Mineralogical composition,

particle size distribution, organic substances and additives can affect the plasticity of clays. Several measuring techniques and devices, like Atterberg, Pfefferkorn, stress/strain curves, indentation, and rheological measurements, are the most used techniques to determine the optimal water content in a clay body required to allow this body to be plastically deformed by shaping [14-19]. In this work the Pfefferkorn method was chosen to evaluate the plasticity of the S1 and S2 stoneware masses. This method is widely accepted in practice and was originally developed for soft silicate ceramic materials [19]. Despite the advance in the theory of the plasticity and the methods of measurement, a common procedure for all types of materials does not exist. The Pfefferkorn method is currently used in routine controls owing to the low cost of the equipment used and the short time required for the tests [20, 21].

In our case the plasticity index was found to be 46.18 for S1 and 52.65 for S2 paste, respectively. Afterwards, the following conclusion should be drawn, both S1 and S2 stoneware pastes present an average impact deformation height, between 4 and 1.25. Regarding the plasticity index, both types of pastes, S1 and S2 are ceramic materials with superior plasticity, the plasticity index is over 30 [22]. Plasticity is not a physical property, but is the result of many properties of clay materials, such as: the size and shape of the material particles, the cohesion between them, the swelling capacity in water, the shrinkage when drying, etc.

Moisture content determination

Plastic raw materials can retain large amounts of water in the form of moisture. For this reason, is necessary to know the humidity to make certain corrections to the manufacturing recipes in case the raw materials are no longer dried before. The moisture content obtained from the analyzes are as follows: 16.85% for S1 and 22.10% for S2 stoneware paste, respectively. Ceramic pastes represent a mixture of solid raw materials with water, the percentage of water varying between 18 and 24% and are used for ceramic household products, tiles, and refractory products whose shaping process involves plastic shaping. The obtained results confirm the fact that the S2 stoneware paste has the necessary humidity to be shaped by plastic processes, such as the potter's wheel.

Drying and firing shrinkages determination

The purpose of this test was to obtain values of shrinkage after drying and firing of stoneware bodies. The drying shrinkage of raw materials and ceramic masses consists in reducing the dimensions of the shaped product

by eliminating the water absorbed on the surface of the particles, in the pores and capillaries of the product. During firing the matrix densifies and shrinkage continues, more vitreous bodies shrink more. The fired shrinkage (shrinkage from dry to fired) is a thus comparative indicator of the degree of vitrification.

The linear shrinkage, LS (%), of dried (LDS) and fired (LFS) samples has been determined by means of the following equation [22]:

$$\text{LDS} = (L_0 - L) / L \times 100 \quad (1)$$

$$\text{LFS} = (L - L_1) / L \times 100 \quad (2)$$

where L_0 , L and L_1 are the diameter (mm) of the green, dried, and fired specimens respectively. Finally, the total shrinkage was calculated, as the sum of the drying and firing shrinkage. The linear shrinkage values obtained for five specimens were averaged for each determination.

LDS for S1 and S2 samples shows similar values of 5.6% and 5.5%, respectively. For S1 the LFS was found to be 7.84, whereas S2 has 6.65%. Finally, the total shrinkage was 13.44% for S1 and 12.15% for S2. With the help of the above experimental data, we concluded that S1 and S2 stoneware samples have high total shrinkage (12÷17%). However, the total shrinkage of a smooth, plastic clay body can be as high as 15%. The most important parameters which affect shrinkage and characteristics of final product are the particle size distribution, chemical and mineralogical composition of raw materials, temperature, and sintering time [23]. In our case, both pastes are recommended to be used to obtain ceramic objects by plastic shaping. Anyway, the clay materials for the ceramic industry with high total shrinkage are not recommended for use in the case of products with a flat shape and narrow dimensional tolerances, due to the large deviations from the nominal dimensions, when fired in industrial furnaces with temperature gradients [22].

CONCLUSIONS

The following conclusions can be drawn from the physical, chemical, mineralogical, and technological characteristics of the studied ceramic pastes:

From the analysis of the results, it appears that the S2 paste has a higher plasticity. This may be due to the higher kaolinite content, which promotes mullite formation on firing and confers plasticity on the green paste facilitating shape-forming operations.

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The mineralogical analysis shows that the S2 ceramic paste after firing contains mullite, which is desirable due to its important properties like low thermal expansion, creep resistance and high temperature stability.

The PSD results show that the S2 paste is composed of much finer constituent particles, with a narrow particle size distribution (PSD).

In conclusion, although both pastes are commercially available and are currently used, according to scientific analyzes and through a careful comparison, we can state that S2 paste is more favorable for processing on the potter's wheel. As we mentioned before, a main advantage is the fact that this paste contains cellulose fibers which can come either from new or recycled paper pulp, making this “greener” than the other ceramic paste.

EXPERIMENTAL SECTION

Materials and methods

Materials

The two types of stoneware used in the experiments are: *Stoneware B17C* (Valentine Clays Ltd, Stoke-on-Trent, UK, sample name: S1) [7] and *PCLI stoneware paper clay* (SIO-2®, Esparreguera-Barcelona, Spain, sample name: S2) [9], respectively.

Methods

The stoneware pastes were characterized from both the chemical-physical and the technological viewpoints using different techniques, as follow.

Particle size distribution (PSD)

Particle size analysis by laser diffraction was performed with a micro and nanoparticle analyzer SALD-7101 (Shimadzu, Japan). The samples were dispersed in a water medium to form a suspension and drawn into the size analyzer. The particles aggregation was reduced using treatment with ultrasounds.

X-ray powder diffraction (XRPD)

The mineralogical composition of the samples before and after firing was determined by XRPD. Pellets of 10 cm diameter were obtained by manual pressing of the paste using a metallic mold. After pressing, the green

ceramic bodies were dried for 24 hours at 105 °C and heat treated in a laboratory furnace at 1260 °C maximum temperature for 20 min. This maximum temperature corresponds to temperature used during firing of industrial ceramic objects.

Prior to analysis, the samples were air-dried and gently ground with the aid of mortar and pestle into powdery form. The crystalline phases were identified using a Bruker D8 Advance (Germany) diffractometer, operating at 40 kV, 40 mA with CuK α radiation ($\lambda = 1.54060 \text{ \AA}$). Scans were conducted from 10 to 80° with a scan rate of 2°/min.

Thermal analysis

Thermoanalytical measurements were conducted on an SDT Q600 (USA) device from T.A. Instruments. Data on thermogravimetry (TG), its derivative (DTG), and differential thermal analysis (DTA) curves, were simultaneously acquired under the following measurement conditions: heating from laboratory temperature to 1300 °C, at a heating rate of 10 °C/min, under normal air atmosphere, using alumina crucibles.

Plasticity determination

The Pfefferkorn method previously described [22] was used to evaluate the plasticity of the two stoneware masses. The Pfefferkorn plastic meter used for the determination is a modified Vicat apparatus in which the needle has been replaced with a metal disc. A defined sample with a diameter of 33 mm and an initial height of 40 mm, produced manually was deformed by a free-falling plate with a mass of 1.192 kg, diameter of 120 mm and 7.5 mm thickness. This measurement was taken with bodies of varying moisture content. The ratios of deformation or the impact deformation heights (H_0 - initial height; H_f - final height) were plotted against the moisture content. From the linear fit of determined points for the two types of pastes, S1 and S2, which express the relation between moisture and impact deformation heights, the corresponding moisture at 3.3 impact deformation height, was found. These represents the Pfefferkorn's plasticity index, the moisture (%) which corresponds to a normal plasticity.

Linear drying and firing shrinkage

The principle of the method consists in marking on the green shaped samples some indentations at a well-established distance and measuring the same distance after drying. Our specimens are made in a mold with a removable bottom in the form of a cube, with a side of 50 mm. The test pieces are marked with two diagonal lines, on which a mark is placed 25 mm from the point of intersection, and then were subjected to a process of gradual drying in an oven. Further, after drying, the samples were heat treated in the furnace at a temperature of 900 °C, for 1-2 h. After firing, the distance between the marks was measured and the firing shrinkage was calculated.

Moisture analyses

The moisture content was determined using the AGS120 Moisture Analyzer (Scientific Industries, NY, USA) which is an electronic device used for quick and precise determination of material humidity upon the basis of weight loss during drying of its small sample (thermo-gravimetric method).

ACKNOWLEDGMENTS

The authors R.B. and L.B. acknowledge the financial support of Partnership for the transfer of innovative technologies and advanced materials in visual arts industry (production, conservation, restoration) - TeMATIC-Art, Project co-financed by FEDR through Competitiveness Operational Programme 2014 – 2020, Funding contract: 14/01.09.2016. The support from SC Bio Nera Plant SA, partner in the project, is also highly acknowledged.

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